Transformation of growing centres. Transformation of anionic ends of living polystyrene to cationic ones and tetrahydrofuran polymerization leading to block copolymer formation

M. Kučera, F. Božek and K. Majerová
Research Institute of Macromolecular Chemistry, Tkalcovská 2, 656 49 *Brno, Czechoslovakia*

(*Received* 3 *February* 1980)

Carbanion growing centres of living polystyrene can react with dicationic silenium initiator with efficiency exceeding 95%. Under suitable conditions one end of the initiator combines with a macroanion while the second preserves its cationic character. Tetrahydrofuran chains can then grow on such transformed centres. In this way a block copolymer of the CAC type is formed. The growth of polytetrahydrofuran on the transformed centre is not identical to the usual homopolymerization growth. Although the rates of both processes are the same, the molecular weights are not. The copolymer thus formed exhibits a molecular weight which obeys the rules valid for living polymers. After addition of more than 100 tetrahydrofuran molecules backbiting reactions can take place on the growing end, leading to the formation of macrocycles The process is repeated periodically. The intitially fast growth of the polytetrahydrofuran chains is probably due to a specific matrix effect of the polystyrene component Steric effects may play a dominant role.

Keywords Polymerization; copolymer; transformation; carbanion; polytetrahydrofuran, polystyrene, steric effects

INTRODUCTION

The transformation of active centres involved in ionic polymerization is important from a theoretical point of view. Moreover, the transformation of anionic centres to cationic ones can offer valuable information about the structure and reactivity of both original and transformed centres as well as about the mechanism of growth. The problem may be even more relevant from the practical standpoint. The polymerization effected on the transformed centres would enable the preparation of block copolymers otherwise not available; it offers the possibilities for the practical application of some types of cationic polymerization which so far have attracted only theoretical attention.

The change of active centre character requires double electron oxidation or reduction to take place during the transformation of ions (single electron transfer effects the transformation of ion to radical and *vice versa*). A double electron transfer from or to an ion cannot take place in a single step. A complicated multistep path leading to the transformation of macroanions to cations has been proposed by Yamashita[1].

A simpler process of anion to cation transformation has been reported by Burgess *et al.*[2-5]. The authors transformed the macroanion to a halogenated derivative by bromine of xylyene dibromide treatment. The polymeric bromide was then converted to a carbocation by $AgClO_4$ or by another superacid silver salt. Burgess *et al.*[6] have also described the transformation of polymeric anions to radicals.

We have noticed that the combination of polymeric ions with low molecular difunctional initiators proceeds with high efficiency (>95%)[7]. The high efficiency of macroion combination has already been observed by Yamashita *et al.*[8] and Richards *et al.*[9]. When one mole of polymeric dianion (dication) is added under suitable conditions to two moles of dication (dianion) initiator, ions possessing opposite charges combine with high efficiency. The initiator molecules which were initially present in excess are attached to polymer ends and the remaining end ions represent new growing centres[10]. An excess of the transforming agent strongly suppresses the combination of the original macroions to block copolymer[7].

Thus the anionic active centres can be transformed to give cationic ones and *vice versa*. The transformation process can be repeated several times. The polymerization carried out on transformed active centres enables nonsymmetrical block copolymers to be obtained. The centre transformation together with macroion combination offers new routes in the field of polymer architecture.

The polymerization of tetrahydrofuran employing initiators whose ion pair enables the shift of the ion pair ⇌ ester equilibrium to the right leads to the formation of macrocycles beside the linear chains. Tetrahydrofuran in the presence of silenium initiator[11] polymerizes without termination and transfer. During this process 4,6-macrocycle molecules are formed per molecule of polymeric dication[12]. We have been interested in the polymerization behaviour of tetrahydrofuran in the presence of active centres formed by the transformation of carbanions (polystyrene dianions) effected by a silenium initiator (silenium = silyl-enium).

0032-3861/82/020207 04$03.00

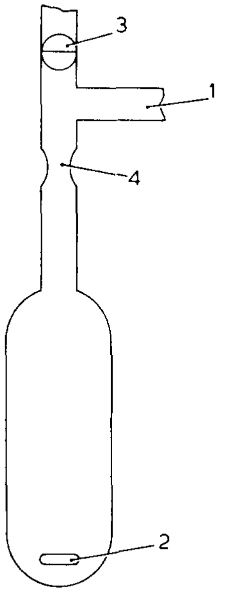


Figure 1 Reactor 1, connection to vacuum line; 2, stirrer; 3, stopcock; 4, seal-off point

EXPERIMENTAL

With the exception of initiator dosage, all operations were carried out using a high vacuum apparatus (10^{-3} – 10^{-4} Pa). The purification of monomers as well as the preparation of initiators has already been described[10–12].

Working procedure and evaluation of results

Known volumes of tetrahydrofuran and styrene were distilled into the reactor shown in *Figure 1*. The solution was cooled down to 243K and sodium salt of tetramer (α-methylstyrene) dianion was introduced into the system by means of a syringe upstream of dry N_2. The styrene polymerization took ~3 s. In this way a good reproducible living polystyrene dianion of almost theoretical molecular weight ($\pm 4\%$) is obtained, the polydispersity coefficient being ≤ 1.2. The solution of living polystyrene was thermostatically controlled at 263K and a benzene solution of silenium dication was added under a stream of dry nitrogen in such an amount that one molecule of silenium dication was present per anion. Immediately upon the introduction of dication the reactor was cooled down in liquid nitrogen, sealed off the line, thermostatically controlled at 263K and left to polymerize for a selected period of time.

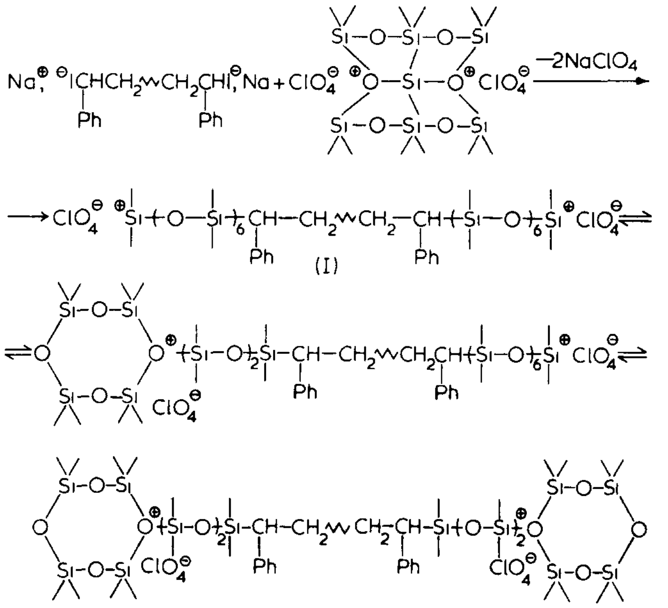
After that the reactor was cut open and its contents transferred into an excess of methanol containing 2% ammonia. The polymer was washed several times (at least 4×) with methanol and dried to constant weight. The polymer yield was 1–12 g depending on tetrahydrofuran conversion (out of this, polystyrene represented 0.73 g).

An attempt was made to extract the dry product with 2-propanol/H_2O (70/30 v/v) mixture or with pure 2-propanol at 333K to remove tetrahydrofuran homopolymer. With the exception of samples polymerized for short times (where copolymer with polystyrene sequences predominated) thick emulsions were always formed.

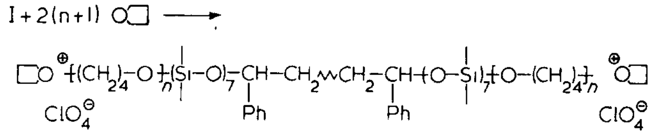
The isolated block copolymer ~bTHF–bS–bTHF~ (CAC = cationic–anionic–cationic) was analysed by a gel permeation chromatograph (g.p.c.) fitted with both u.v. and *RI* detectors.

RESULTS AND DISCUSSION

When polystyrene dianions of molecular weight 5.6×10^3 are brought into contact with the silenium initiator the anionic polystyrene ends are transformed to cationic ones:



Polytetrahydrofuran chains then grow on the transformed centres:



The rate of monomer consumption strictly obeys the relationship derived by Vofsi and Tobolsky[13]. This is documented in *Figure 2* which shows the time dependence of the actual, initial and equilibrium concentrations of tetrahydrofuran ($[M]$, $[M]_0$, $[M]_x$) as well as the concentration of transformed active centres $[I]$ ($\equiv$concentration of silenium initiator) in form of an integrated rate equation. The value of k_p derived from the slope was found to be 7.75×10^{-5} dm^3 mol^{-1} s^{-1} which is in good agreement with k_p measured for tetrahydrofuran polymerization[12] ($k_p = 7.80 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}). The kinetics of tetrahydrofuran polymerization on transformed centres follow the common pattern.

The increase of molecular weight in the case of polytetrahydrofuran formed in the presence of silenium initiator is slower than that calculated according to the rule for the growth of living polymers ($MW = 72.1\,([M]_0 - [M])/[I]$). The reason for this is seen in the formation of macrocycles which coexist with polymeric dications[12]. *Figure 3* demonstrates that during the polymerization on transformed centres there was no simple neutralization of one half of the dication initiator with styrene macroions followed by tetrahydrofuran homopolymerization. The molecular weight of the product increases firstly quite in accordance with the rules valid for living polymer growth. Only after the addition of more than 100 tetrahydrofuran molecules to each dication formed by the transformation does the increase of molecular weight suddenly stop. This might be accounted for by the weakening of the matrix effect due to polystyrene so that the overall mechanism is changed.

During polymerization, the maximum product distribution curve is shifted towards higher molecular weight values. This is apparent from *Figure 4* which shows the traces from both *RI* and u.v. detector. The high molecular weight region of polystyrene containing fraction changes its position several times in the course of polymerization. Initially, the u.v. detector responds almost simultaneously with the *RI* detector; after ~30 h the response of the u.v. detector is suddenly delayed but the delay becomes less pronounced with time. After ~90 h the polystyrene fraction appears suddenly again in the low molecular region (see *Figure 3*). The periodic change of copolymer molecular weight suggests that the growth of polytetrahydrofuran on transformed centres is also a periodic process and alternates with periods of macrocyclic elimination. The whole process seems to be governed by the length of polytetrahydrofuran chains; the growth as well as the formation of cycles takes place almost simultaneously on all centres. This hypothesis is corroborated by the polydispersity coefficients of products (see *Figure 5*). Besides the centre transformation which occurs upon addition of silenium initiator to living polystyrene a mutual combination of diions leading to high-molecular active polystyrene also takes place but to a lesser extent. This process is accompanied by an increase in polydispersity. The living polymerization of

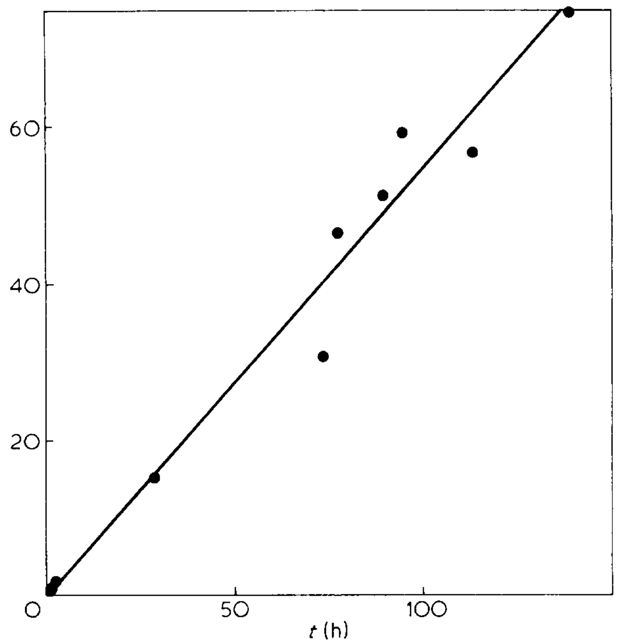


Figure 2 Tetrahydrofuran polymerization on transformed centres. Time dependence of *F*.

$$F = \ln \frac{[M]_0 - [M]_\infty}{[M] - [M]_\infty} \Big/ [I] \ (\text{dm}^3\,\text{mol}^{-1})$$

Concentration (molecular weight) of polystyrene dianion 8.9 mmol dm^{-3} (5.6 x 10^3); temperature of transformation and polymerization 2632K

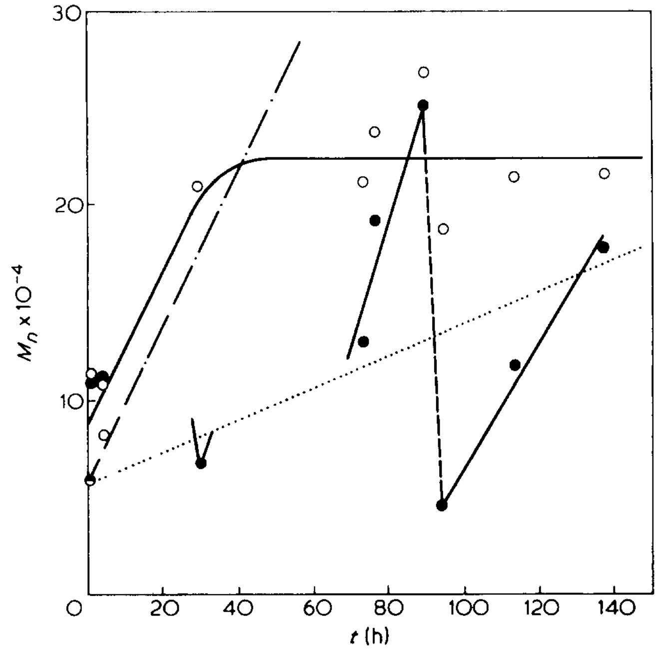


Figure 3 Polymerization of tetrahydrofuran on transformed centres. Dependence of product molecular weight upon time. Concentration (molecular weight) of polystyrene dianion 8.9 mmol dm^{-3} (5.6 x 10^3); temperature of transformation and polymerization 263.2K. Symbols: ○, molecular weight, *RI* detection; ●, molecular weight, u.v. detection; — · — · —, theoretical dependence of M_n for living polymerization; · · · · ·, dependence of M_n found for homopolymerization of tetrahydrofuran[12]

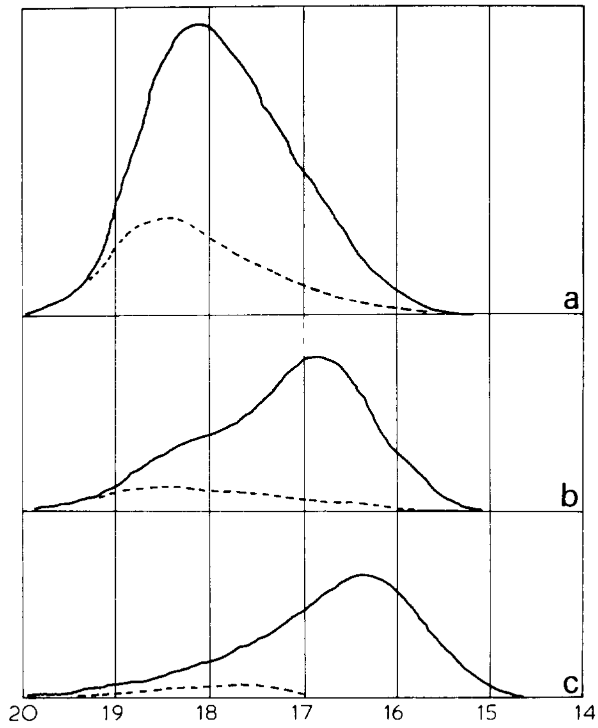


Figure 4 G.p.c. fractogram of polymerization product formed on transformed centres. Polymerization time (h). (a) 4; (b) 29; (c) 137. ——, *RI* detector; — — — —, u.v. detector

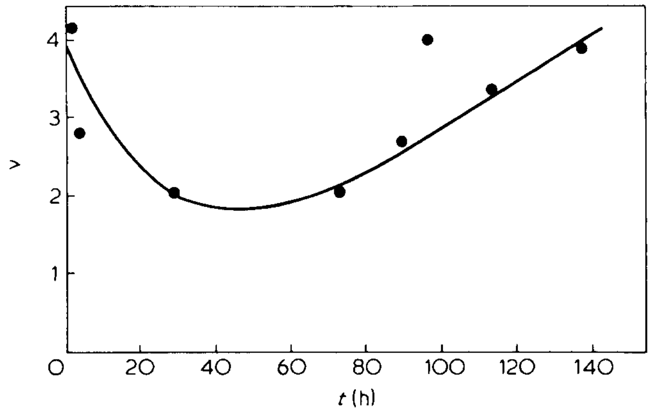


Figure 5 Time dependence of the polydispersity coefficient of the product of polymerization on transformed centres

tetrahydrofuran proceeds at the same rate on all centres. The relative chain length becomes uniform and the polydispersity coefficient decreases. As soon as macrocycles are eliminated from polytetrahydrofuran blocks the molecular weight distribution is broadened again.

ACKNOWLEDGEMENTS

The authors wish to thank Dr Lániková for molecular weight determination of polymerization products by g.p.c.

REFERENCES

1 Yamashita, Y. *Polym. Prepr.* 1972, **13**, 539
2 Burgess, F. J., Cunliffe, A. V., Richards, D. H. and Sherrington, D. C. *J. Polym. Sci. (Polym. Lett. Edn.)* 1976, **14**, 471
3 Burgess, F. J., Cunliffe, A. V., MacCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 719
4 Burgess, F. J., Cunliffe, A. V., MacCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 726
5 Burgess, F. J., Cunliffe, A. V., Dawkins, J. W. and Richards, D. H. *Polymer* 1977, **18**, 733
6 Burgess, F. J., Cunliffe, A. V. and Richards, D. H. *J. Polym. Sci. (Polym. Lett. Edn.)* 1976, **14**, 477
7 Kučera, M., Božek, F. and Majerová, K. *Polymer* 1979, **20**, 1013
8 Yamashita, Y., Nobutoki, K., Nakamura, Y. and Hirota, M. *Macromolecules* 1971, **4**, 548
9 Richards, D. H., Kingston, S. B. and Souel, T. *Polymer* 1978, **19**, 68
10 Kučera, M., Majerová, K. and Božek, F. *Czech. Pat. Appl.* 4110-77, June 22, 1977
11 Kučera, M. and Kelblerová, H. *Collect. Czech. Chem. Commun.* 1979, **44**, 542
12 Kučera, M., Božek, F. and Majerová, K. *Polymer* in press
13 Vofsi, D. and Tobolsky, A. V. *J. Polym Sci. (A)* 1965, **3**, 3261